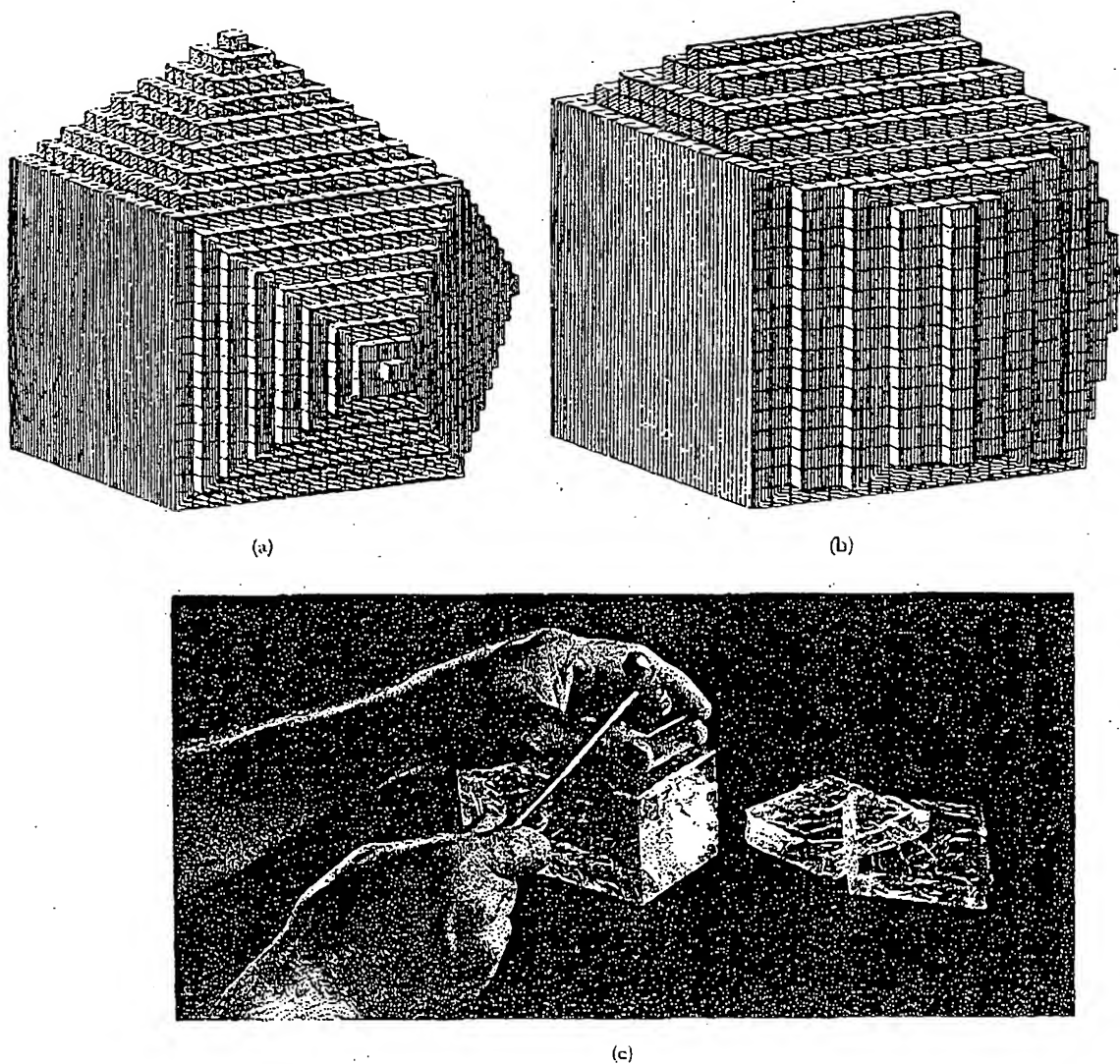(a)

(b)

(c)

Figure 1 Relation of the external form of crystals to the form of the elementary building blocks. The building blocks are identical in (a) and (b), but different crystal faces are developed. (c) Cleaving a crystal of rocksalt.

2

CHAPTER 1: CRYSTAL STRUCTURE

Solid state physics is largely concerned with crystals and electrons in crystals. The study of solid state physics began in the early years of this century following the discovery of x-ray diffraction by crystals and the publication of a series of simple calculations and successful predictions of the properties of crystals.

When a crystal grows in a constant environment, the form develops as if identical building blocks were added continuously (Fig. 1). The building blocks are atoms or groups of atoms, so that a crystal is a three-dimensional periodic array of atoms.

This was known in the 18th century when mineralogists discovered that the index numbers of the directions of all faces of a crystal are exact integers. Only the arrangement of identical particles in a periodic array can account for the law of integral indices,[1] as discussed below.

In 1912 a paper entitled "Interference effects with Röntgen rays" was presented to the Bavarian Academy of Sciences in Munich. In the first part of the paper, Laue developed an elementary theory of the diffraction of x-rays by a periodic array. In the second part, Friedrich and Knipping reported the first experimental observations of x-ray diffraction by crystals.[2]

The work proved decisively that crystals are composed of a periodic array of atoms. With an established atomic model of a crystal, physicists now could think much further. The studies have been extended to include amorphous or noncrystalline solids, glasses, and liquids. The wider field is known as condensed matter physics, and it is now the largest and probably the most vigorous area of physics.

PERIODIC ARRAYS OF ATOMS

An ideal crystal is constructed by the infinite repetition of identical structural units in space. In the simplest crystals the structural unit is a single atom, as in copper, silver, gold, iron, aluminum, and the alkali metals. But the smallest structural unit may comprise many atoms or molecules.

The structure of all crystals can be described in terms of a lattice, with a group of atoms attached to every lattice point. The group of atoms is called the basis; when repeated in space it forms the crystal structure.

[1] R. J. Haüy, *Essai d'une théorie sur la structure des cristaux*. Paris, 1784; *Traité de cristallographie*. Paris, 1801.

[2] For personal accounts of the early years of x-ray diffraction studies of crystals, see P. P. Ewald, ed., *Fifty years of x-ray diffraction*. A. Oosthoek's Uitgeversmij., Utrecht, 1962.

Lattice Translation Vectors

The lattice is defined by three fundamental translation vectors a_1, a_2, a_3 such that the atomic arrangement looks the same in every respect when viewed from the point r as when viewed from the point

$$r' = r + u_1a_1 + u_2a_2 + u_3a_3 , \tag{1}$$

where u_1, u_2, u_3 are arbitrary integers. The set of points r' defined by (1) for all u_1, u_2, u_3 defines a lattice.

A lattice is a regular periodic array of points in space. (The analog in two dimensions is called a net, as in Chapter 18.) A lattice is a mathematical abstraction; the crystal structure is formed when a basis of atoms is attached identically to every lattice point. The logical relation is

$$\text{lattice} + \text{basis} = \text{crystal structure} . \tag{2}$$

The lattice and the translation vectors a_1, a_2, a_3 are said to be primitive if any two points r, r' from which the atomic arrangement looks the same always satisfy (1) with a suitable choice of the integers u_1, u_2, u_3. With this definition of the primitive translation vectors, there is no cell of smaller volume that can serve as a building block for the crystal structure.

We often use primitive translation vectors to define the crystal axes. However, nonprimitive crystal axes are often used when they have a simpler relation to the symmetry of the structure. The crystal axes a_1, a_2, a_3 form three adjacent edges of a parallelepiped. If there are lattice points only at the corners, then it is a primitive parallelepiped.

A lattice translation operation is defined as the displacement of a crystal by a crystal translation vector

$$T = u_1a_1 + u_2a_2 + u_3a_3 . \tag{3}$$

Any two lattice points are connected by a vector of this form.

To describe a crystal structure, there are three important questions to answer: What is the lattice? What choice of a_1, a_2, a_3 do we wish to make? What is the basis?

More than one lattice is always possible for a given structure, and more than one set of axes is always possible for a given lattice. The basis is identified once these choices have been made. Everything (including the x-ray diffraction pattern) works out correctly in the end provided that (3) has been satisfied.

The symmetry operations of a crystal carry the crystal structure into itself. These include the lattice translation operations. Further, there are rotation and reflection operations, called **point operations**. About lattice points or certain special points within an elementary parallelepiped it may be possible to apply rotations and reflections that carry the crystal into itself.

Finally, there may exist compound operations made up of combined translation and point operations. Textbooks on crystallography are largely devoted to
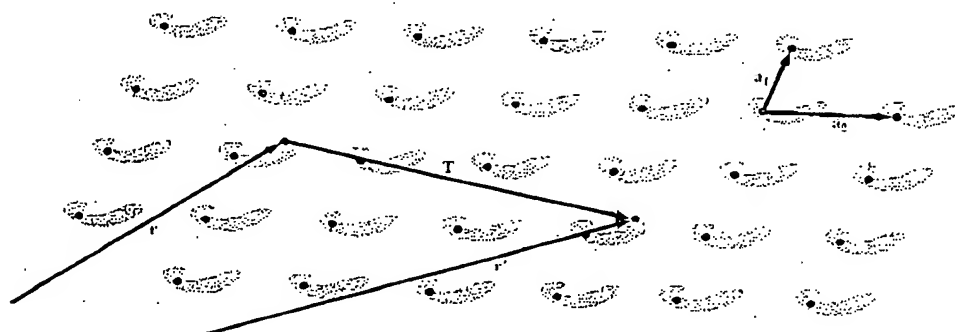
Figure 2 Portion of a crystal of an imaginary protein molecule, in a two-dimensional world. (We picked a protein molecule because it is not likely to have a special symmetry of its own.) The atomic arrangement in the crystal looks exactly the same to an observer at r' as to an observer at r, provided that the vector T which connects r' and r may be expressed as an integral multiple of the vectors a_1 and a_2. In this illustration, $T = -a_1 + 3a_2$. The vectors a_1 and a_2 are primitive translation vectors of the two-dimensional lattice.
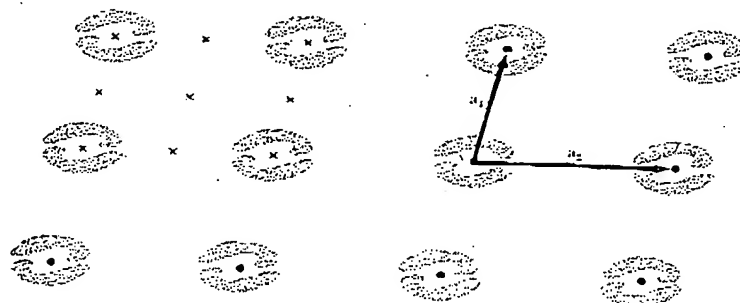

Figure 3 Similar to Fig. 2, but with protein molecules associated in pairs. The crystal translation vectors are a_1 and a_2. A rotation of π radians about any point marked $\times$ will carry the crystal into itself. This occurs also for equivalent points in other cells, but we have marked the points $\times$ only within one cell.

the description of symmetry operations. The crystal structure of Fig. 2 is drawn to have only translational symmetry operations. The crystal structure of Fig. 3 allows both translational and point symmetry operations.

Basis and the Crystal Structure

A basis of atoms is attached to every lattice point, with every basis identical in composition, arrangement, and orientation. Figure 4 shows how a crystal structure is formed by adding a basis to every lattice point. The lattice is indicated by dots in Figs. 2 and 3, but in Fig. 4c the dots are omitted.
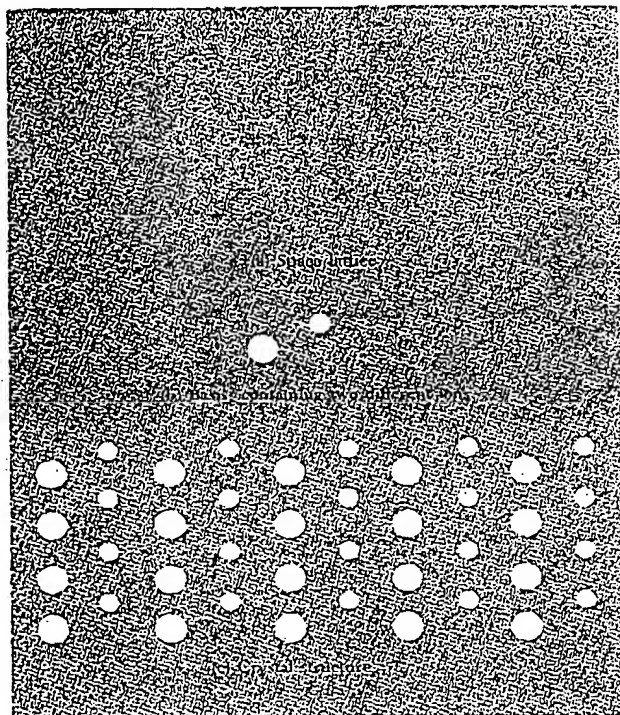
Figure 4 The crystal structure is formed by the addition of the basis (b) to every lattice point of the lattice (a). By looking at (c), you can recognize the basis and then you can abstract the space lattice. It does not matter where the basis is put in relation to a lattice point.

The number of atoms in the basis may be one, or it may be more than one. The position of the center of an atom j of the basis relative to the associated lattice point is

$$r_j = x_j a_1 + y_j a_2 + z_j a_3 \qquad (4)$$

We may arrange the origin, which we have called the associated lattice point, so that $0 \leq x_j, y_j, z_j \leq 1$.

Primitive Lattice Cell

The parallelepiped defined by primitive axes a_1, a_2, a_3 is called a **primitive cell** (Fig. 5b). A primitive cell is a type of cell or unit cell. (The adjective unit is superfluous and not needed.) A cell will fill all space by the repetition of suitable crystal translation operations. A primitive cell is a minimum-volume cell.

There are many ways of choosing the primitive axes and primitive cell for a given lattice. The number of atoms in a primitive cell or primitive basis is always the same for a given crystal structure.
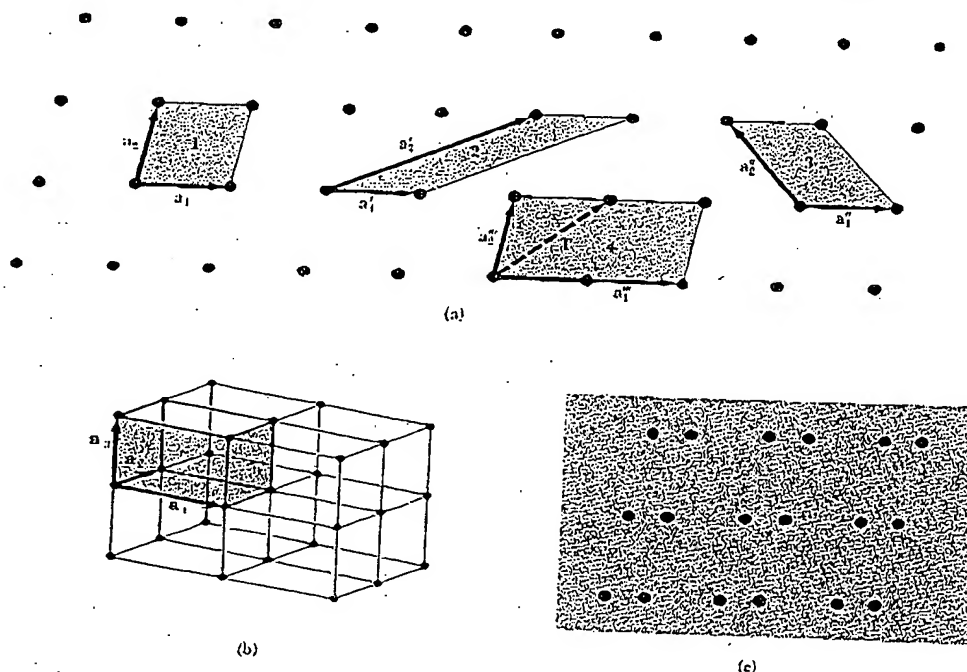
(a)

(b)

(c)

Figure 5a   Lattice points of a space lattice in two dimensions. All pairs of vectors a_1, a_2 are translation vectors of the lattice. But a_1''', a_2''' are not primitive translation vectors because we cannot form the lattice translation T from integral combinations of a_1''' and a_2'''. All other pairs shown of a_1 and a_2 may be taken as the primitive translation vectors of the lattice. The parallelograms 1, 2, 3 are equal in area and any of them could be taken as the primitive cell. The parallelogram 4 has twice the area of a primitive cell.

Figure 5b   Primitive cell of a space lattice in three dimensions.

Figure 5c   Suppose these points are identical atoms: sketch in on the figure a set of lattice points, a choice of primitive axes, a primitive cell, and the basis of atoms associated with a lattice point.

There is always one lattice point per primitive cell. If the primitive cell is a parallelepiped with lattice points at each of the eight corners, each lattice point is shared among eight cells, so that the total number of lattice points in the cell is one: $8 \times \frac{1}{8} = 1$.

The volume of a parallelepiped with axes a_1, a_2, a_3 is

$$V_c = |a_1 \cdot a_2 \times a_3| ,\tag{5}$$

by elementary vector analysis. The basis associated with a primitive cell is called a primitive basis. No basis contains fewer atoms than a primitive basis contains.
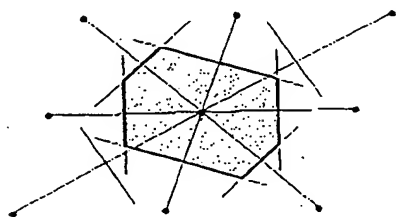
Figure 6 A primitive cell may also be chosen following this procedure: (1) draw lines to connect a given lattice point to all nearby lattice points; (2) at the midpoint and normal to these lines, draw new lines or planes. The smallest volume enclosed in this way is the Wigner-Seitz primitive cell. All space may be filled by these cells, just as by the cells of Fig. 5.

Another way of choosing a primitive cell is shown in Fig. 6. This is known to physicists as a **Wigner-Seitz cell**.

FUNDAMENTAL TYPES OF LATTICES

Crystal lattices can be carried or mapped into themselves by the lattice translations T and by various other symmetry operations. A typical symmetry operation is that of rotation about an axis that passes through a lattice point. Lattices can be found such that one-, two-, three-, four-, and sixfold rotation axes carry the lattice into itself, corresponding to rotations by 2π, $2\pi/2$, $2\pi/3$, $2\pi/4$, and $2\pi/6$ radians and by integral multiples of these rotations. The rotation axes are denoted by the symbols 1, 2, 3, 4, and 6.

We cannot find a lattice that goes into itself under other rotations, such as by $2\pi/7$ radians or $2\pi/5$ radians. A single molecule properly designed can have any degree of rotational symmetry, but an infinite periodic lattice cannot. We can make a crystal from molecules that individually have a fivefold rotation axis, but we should not expect the lattice to have a fivefold rotation axis. In Fig. 7 we show what happens if we try to construct a periodic lattice having fivefold symmetry: the pentagons do not fit together to fill all space, showing that we cannot combine fivefold point symmetry with the required translational periodicity.

By lattice point group we mean the collection of symmetry operations which, applied about a lattice point, carry the lattice into itself. The possible rotations have been listed. We can have mirror reflections m about a plane through a lattice point. The inversion operation is composed of a rotation of π followed by reflection in a plane normal to the rotation axis; the total effect is to replace r by $-r$. The symmetry axes and symmetry planes of a cube are shown in Fig. 8.

Two-Dimensional Lattice Types

There is an unlimited number of possible lattices because there is no natural restriction on the lengths of the lattice translation vectors or on the angle φ between them. The lattice in Fig. 5a was drawn for arbitrary a_1 and a_2. A general lattice such as this is known as an **oblique lattice** and is invariant only under rotation of π and 2π about any lattice point.

Figure 7 A fivefold axis of symmetry cannot exist in a periodic lattice because it is not possible to fill the area of a plane with a connected array of pentagons. We can, however, fill all the area of a plane with just two distinct designs of "tiles" or elementary polygons. A quasicrystal is a quasiperiodic nonrandom assembly of two types of figures. Quasicrystals are discussed at the end of Chapter 2.
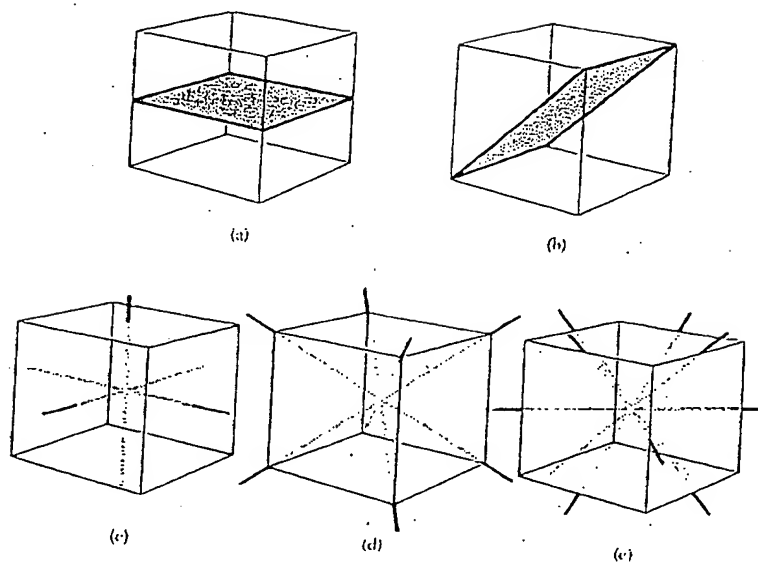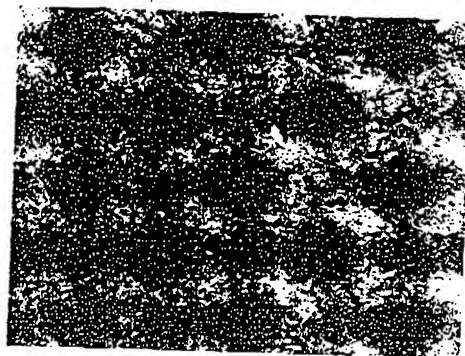
(a)　　　　　(b)

(c)　　　　(d)　　　　(e)

Figure 8 (a) A plane of symmetry parallel to the faces of a cube. (b) A diagonal plane of symmetry in a cube. (c) The three tetrad axes of a cube. (d) The four triad axes of a cube. (e) The six diad axes of a cube.

But special lattices of the oblique type can be invariant under rotation of $2\pi/3$, $2\pi/4$, or $2\pi/6$, or under mirror reflection. We must impose restrictive conditions on a_1 and a_2 if we want to construct a lattice that will be invariant under one or more of these new operations. There are four distinct types of restriction, and each leads to what we may call a special lattice type. Thus there are five distinct lattice types in two dimensions, the oblique lattice and the four special lattices shown in Fig. 9. Bravais lattice is the common phrase for a distinct lattice type; we say that there are five Bravais lattices or nets in two dimensions.

Three-Dimensional Lattice Types

The point symmetry groups in three dimensions require the 14 different lattice types listed in Table 1. The general lattice is triclinic, and there are 13 special lattices. These are grouped for convenience into systems classified according to seven types of cells, which are triclinic, monoclinic, orthorhombic, tetragonal, cubic, trigonal, and hexagonal. The division into systems is expressed in the table in terms of the axial relations that describe the cells.

The cells in Fig. 10 are conventional cells; of these only the sc is a primitive cell. Often a nonprimitive cell has a more obvious relation with the point symmetry operations than has a primitive cell.

Table 1   The 14 lattice types in three dimensions

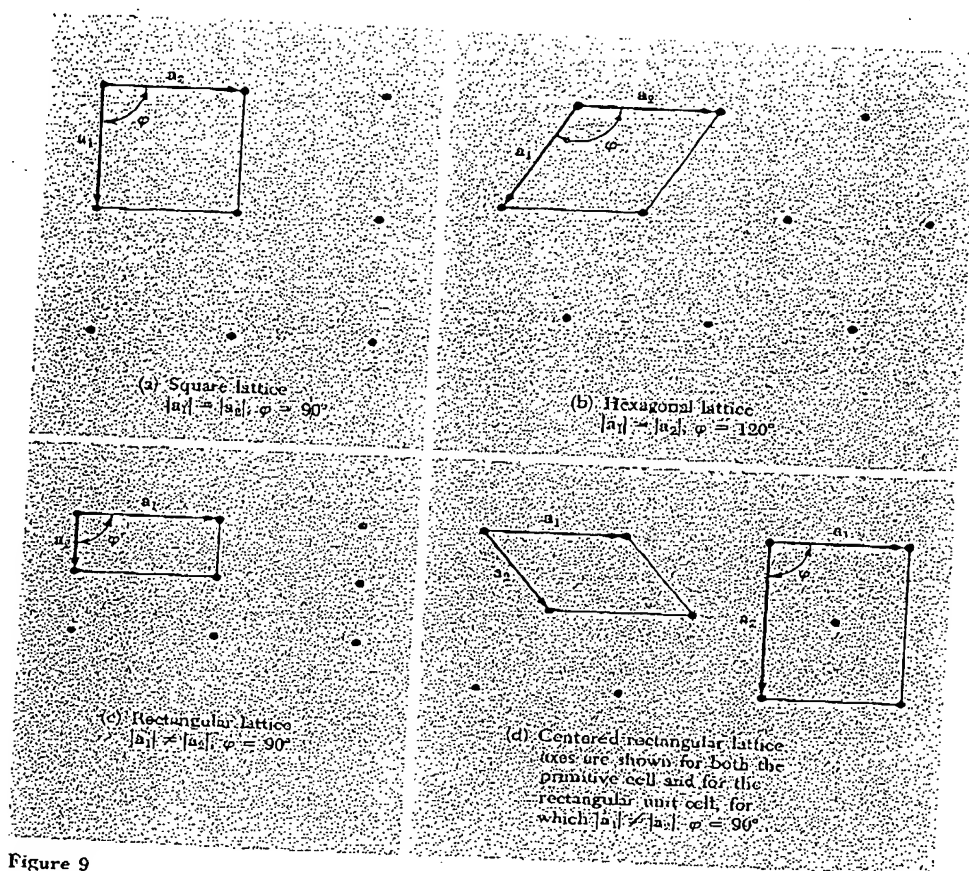| System	Number of lattices	Restrictions on conventional cell axes and angles
Triclinic	1	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$ $\alpha = \gamma = 90° \neq \beta$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$
Cubic	3	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90°$
Trigonal	1	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120°, \neq 90°$
Hexagonal	1	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90°$ $\gamma = 120°$

of
e
it
of
c
ir
a
o.

nt
l3
c-
c,
x-

ni-
nt

90°

(a) Square lattice
$|a_1| = |a_2|; \varphi = 90°$

(b) Hexagonal lattice
$|a_1| = |a_2|; \varphi = 120°$

(c) Rectangular lattice
$|a_1| \neq |a_2|; \varphi = 90°$

(d) Centered rectangular lattice
axes are shown for both the
primitive cell and for the
rectangular unit cell, for
which $|a_1| \neq |a_2|; \varphi = 90°$.

Figure 9

sc   bcc   fcc
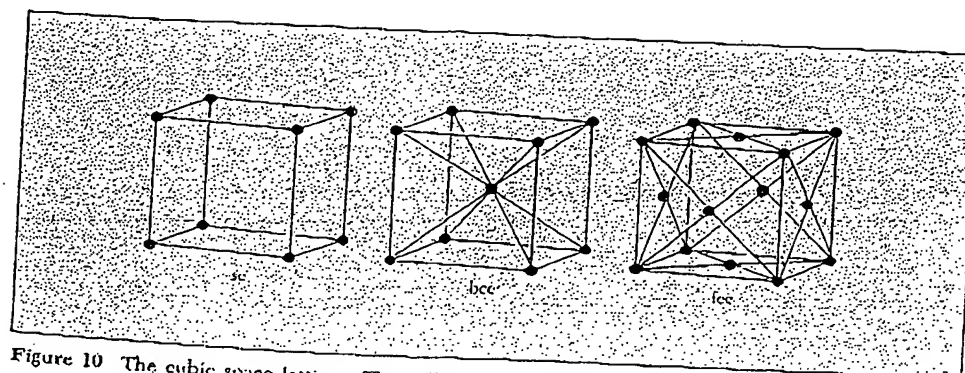
Figure 10   The cubic space lattices. The cells shown are the conventional cells.

Table 2 Characteristics of cubic lattices[a]

	Simple	Body-centered	Face-centered
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors[a]	6	8	12
Nearest-neighbor distance	a	$3^{1/2}a/2 = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	a	a
Packing fraction[b]	$\frac{1}{6}\pi$ $= 0.524$	$\frac{1}{8}\pi\sqrt{3}$ $= 0.680$	$\frac{1}{6}\pi\sqrt{2}$ $=0.740$

[a]Tables of numbers of neighbors and distances in sc, bcc, fcc, hcp, and diamond structures are given on pp. 1037–1039 of J. Hirschfelder, C. F. Curtis and R. B. Bird, *Molecular theory of gases and liquids*, Wiley, 1964.

[b]The packing fraction is the maximum proportion of the available volume that can be filled with hard spheres.

There are three lattices in the cubic system: the simple cubic (sc) lattice, the body-centered cubic (bcc) lattice, and the face-centered cubic (fcc) lattice. The characteristics of the three cubic lattices are summarized in Table 2.

A primitive cell of the bcc lattice is shown in Fig. 11, and the primitive translation vectors are shown in Fig. 12. The primitive translation vectors of the fcc lattice are shown in Fig. 13. Primitive cells by definition contain only one lattice point, but the conventional bcc cell contains two lattice points, and the fcc cell contains four lattice points.

The position of a point in a cell is specified by (4) in terms of the atomic coordinates x, y, z. Here each coordinate is a fraction of the axial length a_1, a_2, a_3 in the direction of the coordinate axis, with the origin taken at one corner of the cell. Thus the coordinates of the body center of a cell are $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, and the face centers include $\frac{1}{2}\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$.

In the hexagonal system the primitive cell is a right prism based on a rhombus with an included angle of 120°. Figure 14 shows the relationship of the rhombic cell to a hexagonal prism.

INDEX SYSTEM FOR CRYSTAL PLANES

The orientation of a crystal plane is determined by three points in the plane, provided they are not collinear. If each point lay on a different crystal axis, the plane could be specified by giving the coordinates of the points in terms of the lattice constants a_1, a_2, a_3.
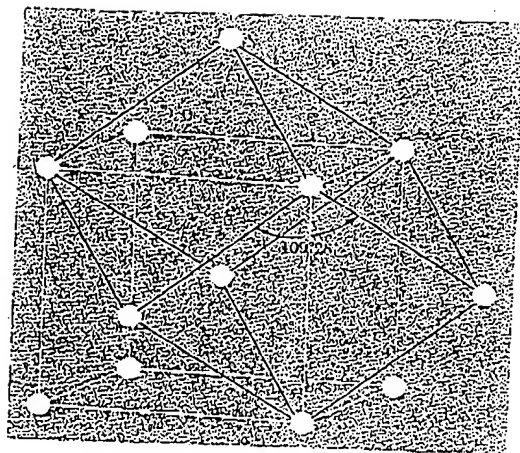
Figure 11 Body-centered cubic lattice, showing a primitive cell. The primitive cell shown is a rhombohedron of edge $\frac{1}{2}\sqrt{3}\,a$, and the angle between adjacent edges is 109°28′.
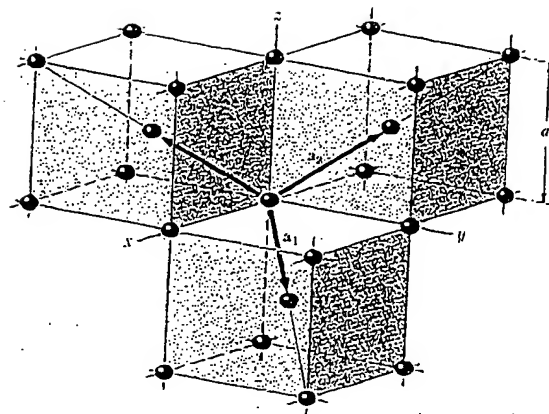

Figure 12 Primitive translation vectors of the body-centered cubic lattice; these vectors connect the lattice point at the origin to lattice points at the body centers. The primitive cell is obtained on completing the rhombohedron. In terms of the cube edge a the primitive translation vectors are

$$\mathbf{a}_1 = \tfrac{1}{2}a(\hat{x} + \hat{y} - \hat{z})\;; \qquad \mathbf{a}_2 = \tfrac{1}{2}a(-\hat{x} + \hat{y} + \hat{z})\;;$$

$$\mathbf{a}_3 = \tfrac{1}{2}a(\hat{x} - \hat{y} + \hat{z})\;.$$
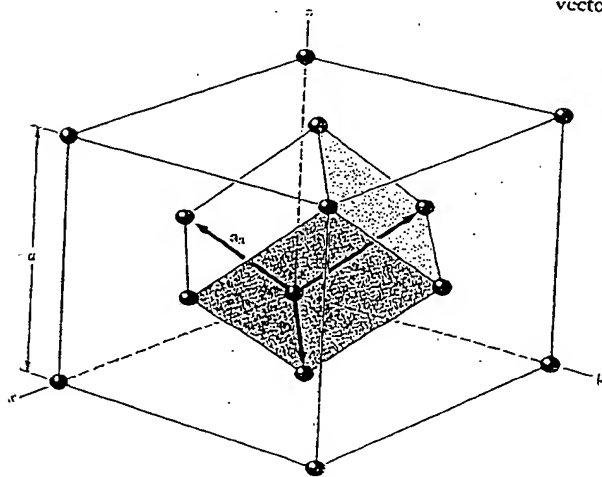
Figure 13 The rhombohedral primitive cell of the face-centered cubic crystal. The primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ connect the lattice point at the origin with lattice points at the face centers. As drawn, the primitive vectors are:

$$\mathbf{a}_1 = \tfrac{1}{2}a(\hat{x} + \hat{y})\;; \qquad \mathbf{a}_2 = \tfrac{1}{2}a(\hat{y} + \hat{z})\;; \qquad \mathbf{a}_3 = \tfrac{1}{2}a(\hat{z} + \hat{x})\;.$$

The angles between the axes are 60°. Here $\hat{x}$, $\hat{y}$, $\hat{z}$ are the Cartesian unit vectors.
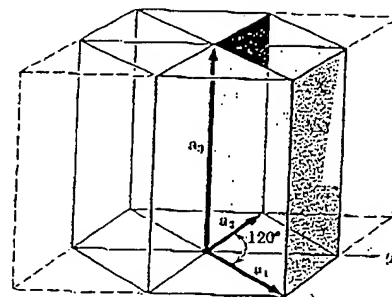

Figure 14 Relation of the primitive cell in the hexagonal system (heavy lines) to a prism of hexagonal symmetry. Here $a_1 = a_2 \neq a_3$.
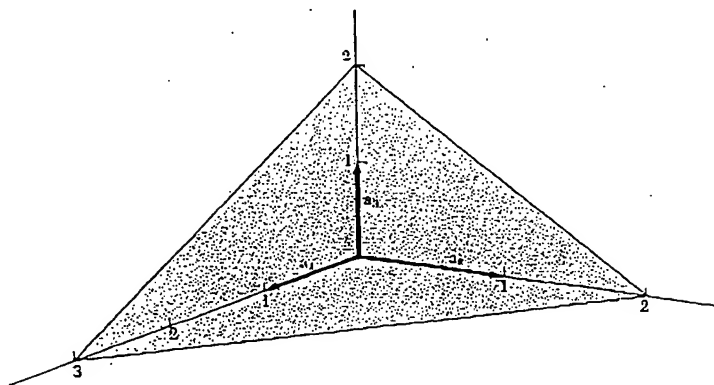
14

Figure 15 This plane intercepts the a_1, a_2, a_3 axes at $3a_1$, $2a_2$, $2a_3$. The reciprocals of these numbers are $\frac{1}{3}$, $\frac{1}{2}$, $\frac{1}{2}$. The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (233).

However, it turns out to be more useful for structure analysis to specify the orientation of a plane by the indices determined by the following rules (Fig. 15).

- Find the intercepts on the axes in terms of the lattice constants a_1, a_2, a_3. The axes may be those of a primitive or nonprimitive cell.
- Take the reciprocals of these numbers and then reduce to three integers having the same ratio, usually the smallest three integers. The result, enclosed in parentheses (hkl), is called the index of the plane.

For the plane whose intercepts are 4, 1, 2, the reciprocals are $\frac{1}{4}$, 1, and $\frac{1}{2}$; the smallest three integers having the same ratio are (142). For an intercept at infinity, the corresponding index is zero. The indices of some important planes in a cubic crystal are illustrated by Fig. 16.

The indices (hkl) may denote a single plane or a set of parallel planes. If a plane cuts an axis on the negative side of the origin, the corresponding index is negative, indicated by placing a minus sign above the index: $(h\bar{k}l)$. The cube faces of a cubic crystal are (100), (010), (001), ($\bar{1}$00), ($0\bar{1}0$), and ($00\bar{1}$). Planes equivalent by symmetry may be denoted by curly brackets (braces) around indices; the set of cube faces is {100}. When we speak of the (200) plane we mean a plane parallel to (100) but cutting the a_1 axis at $\frac{1}{2}a$.

The indices $[uvw]$ of a direction in a crystal are the set of the smallest integers that have the ratio of the components of a vector in the desired direction, referred to the axes. The a_1 axis is the [100] direction; the $-a_2$ axis is the
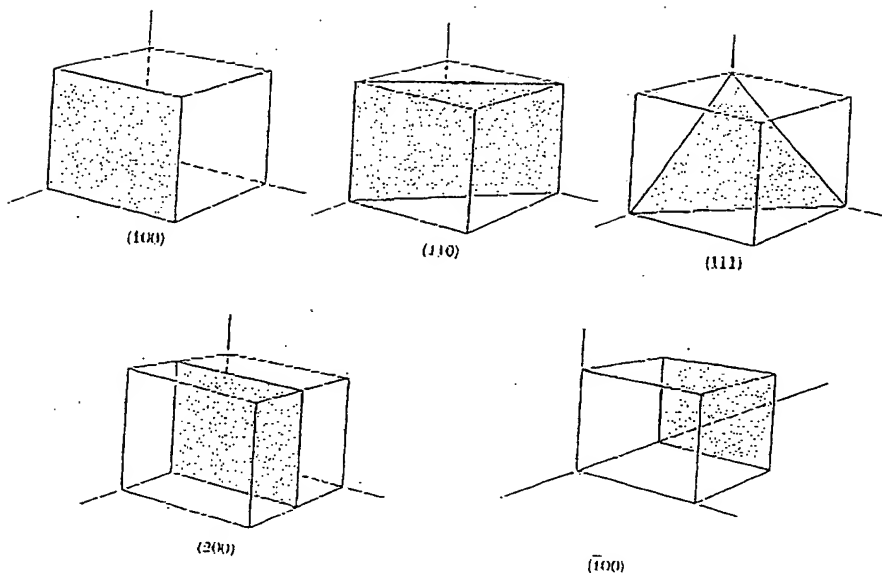
Figure 16 Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to (Ī00).

[0Ī0] direction. In cubic crystals the direction [hkl] is perpendicular to a plane (hkl) having the same indices, but this is not generally true in other crystal systems.

SIMPLE CRYSTAL STRUCTURES

We discuss simple crystal structures of general interest: the sodium chloride, cesium chloride; hexagonal close-packed, diamond, and cubic zinc sulfide structures.

Sodium Chloride Structure

The sodium chloride, NaCl, structure is shown in Figs. 17 and 18. The lattice is face-centered cubic; the basis consists of one Na atom and one Cl atom separated by one-half the body diagonal of a unit cube. There are four units of NaCl in each unit cube, with atoms in the positions

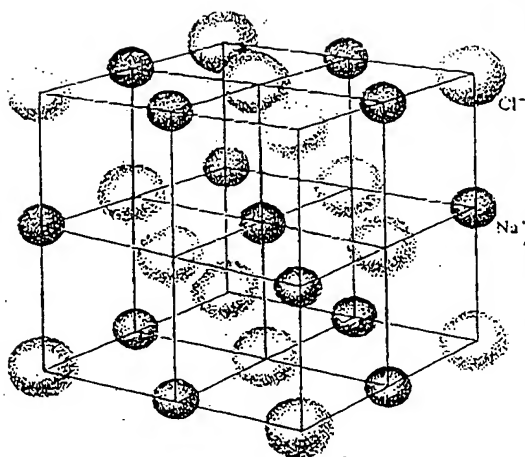| Cl:	000	$\frac{1}{2}\frac{1}{2}0$	$\frac{1}{2}0\frac{1}{2}$	$0\frac{1}{2}\frac{1}{2}$
Na:	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	$00\frac{1}{2}$	$0\frac{1}{2}0$	$\frac{1}{2}00$

Figure 17 · We may construct the sodium chloride crystal structure by arranging Na^+ and Cl^- ions alternately at the lattice points of a simple cubic lattice. In the crystal each ion is surrounded by six nearest neighbors of the opposite charge. The space lattice is fcc, and the basis has one Cl^- ion at 000 and one Na^+ ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The figure shows one conventional cubic cell. The ionic diameters here are reduced in relation to the cell in order to clarify the spatial arrangement.
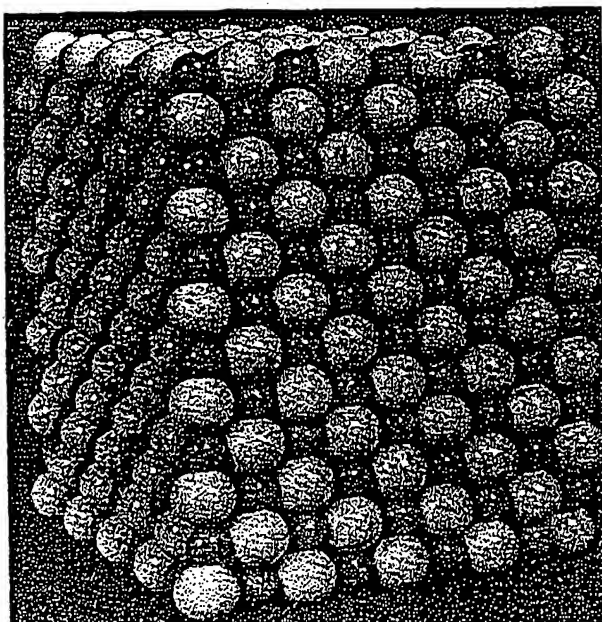
Figure 18 Model of sodium chloride. The sodium ions are smaller than the chlorine ions. (Courtesy of A. N. Holden and P. Singer.)

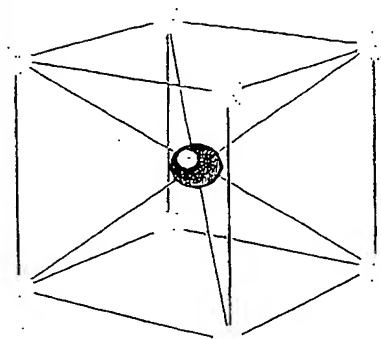Figure 19 Natural crystals of lead sulfide, PbS, which has the NaCl crystal structure. (Photograph by B. Burleson.)

Figure 20 The cesium chloride crystal structure. The space lattice is simple cubic, and the basis has one Cs^+ ion at 000 and one Cl^- ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

Each atom has as nearest neighbors six atoms of the opposite kind. Representative crystals having the NaCl arrangement include those in the following table. The cube edge a is given in angstroms; $1 \text{ Å} \equiv 10^{-8} \text{ cm} \equiv 10^{-10} \text{ m} \equiv 0.1 \text{ nm}$.

Crystal	a	Crystal	a
LiH	4.08 Å	AgBr	5.77 Å
MgO	4.20	PbS	5.92
MnO	4.43	KCl	6.29
NaCl	5.63	KBr	6.59

Figure 19 is a photograph of crystals of lead sulfide (PbS) from Joplin, Missouri. The Joplin specimens form in beautiful cubes.

Cesium Chloride Structure

The cesium chloride structure is shown in Fig. 20. There is one molecule per primitive cell, with atoms at the corners 000 and body-centered positions $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ of the simple cubic space lattice. Each atom may be viewed as at the center of a cube of atoms of the opposite kind, so that the number of nearest neighbors or coordination number is eight.

Crystal	a	Crystal	a
BeCu	2.70 Å	LiHg	3.29 Å
AlNi	2.88	NH₄Cl	3.87
CuZn (β-brass)	2.94	TlBr	3.97
CuPd	2.99	CsCl	4.11
AgMg	3.28	TlI	4.20

Hexagonal Close-packed Structure (hcp)

There are an infinite number of ways of arranging identical spheres in a regular array that maximizes the packing fraction (Fig. 21). One is the face-centered cubic structure; another is the hexagonal close-packed structure (Fig. 22). The fraction of the total volume occupied by the spheres is 0.74 for both structures. No structure, regular or not, has denser packing.

Spheres are arranged in a single closest-packed layer A by placing each sphere in contact with six others. This layer may serve as either the basal plane of an hcp structure or the (111) plane of the fcc structure. A second similar layer B may be added by placing each sphere of B in contact with three spheres of the bottom layer, as in Fig. 21. A third layer C may be added in two ways. We obtain the fcc structure if the spheres of the third layer are added over the holes in the first layer that are not occupied by B. We obtain the hcp structure when the spheres in the third layer are placed directly over the centers of the spheres in the first layer.
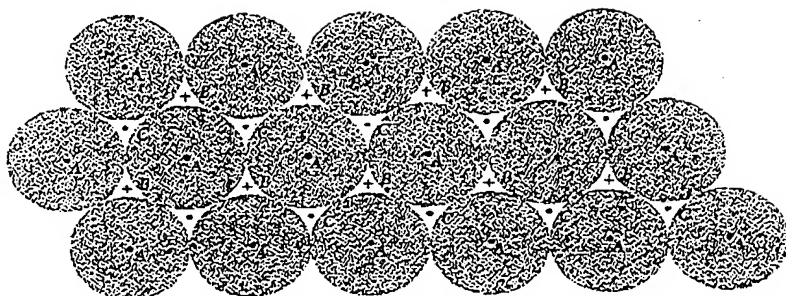
Figure 21 A close-packed layer of spheres is shown, with centers at points marked A. A second and identical layer of spheres can be placed on top of this, above and parallel to the plane of the drawing, with centers over the points marked B. There are two choices for a third layer. It can go in over A or over C. If it goes in over A the sequence is ABABAB. . . and the structure is hexagonal close-packed. If the third layer goes in over C the sequence is ABCABCABC. . . and the structure is face-centered cubic.
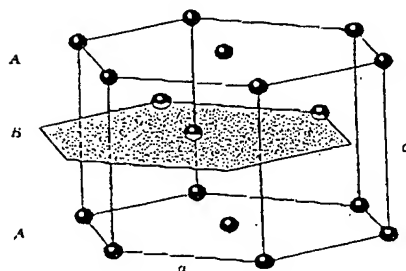

Figure 22 The hexagonal close-packed structure. The atom positions in this structure do not constitute a space lattice. The space lattice is simple hexagonal with a basis of two identical atoms associated with each lattice point. The lattice parameters a and c are indicated, where a is in the basal plane and c is the magnitude of the axis a_3 of Fig. 14.
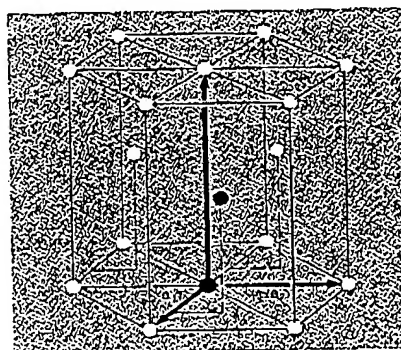

Figure 23 The primitive cell has $a_1 = a_2$, with an included angle of 120°. The c axis (or a_3) is normal to the plane of a_1 and a_2. The ideal hcp structure has $c = 1.633\, a$. The two atoms of one basis are shown as solid circles. One atom of the basis is at the origin; the other atom is at $\frac{2}{3}\frac{1}{3}\frac{1}{2}$, which means at the position $r = \frac{2}{3}a_1 + \frac{1}{3}a_2 + \frac{1}{2}a_3$.

The hcp structure has the primitive cell of the hexagonal lattice, but with a basis of two atoms (Fig. 23). The fcc primitive cell has a basis of one atom (Fig. 13).

The ratio c/a (or a_3/a_1) for hexagonal closest-packing of spheres has the value $(\frac{8}{3})^{1/2} = 1.633$, as in Problem 3. It is usual to refer to crystals as hcp even if the actual c/a ratio departs somewhat from this theoretical value.

The number of nearest-neighbor atoms is 12 for both hcp and fcc structures. If the binding energy (or free energy) depended only on the number of